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Degradation studies of spray coated polymer films using cantilever sensors[i]

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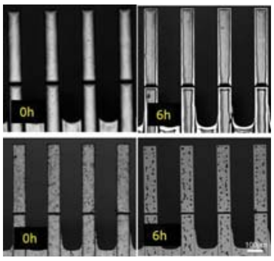
Micromechanical sensors (cantilevers & strings) are versatile characterization tools for polymers

Miniaturized samples allow for fast and precise characterization of polymer degradation processes

Thin polymer layer are placed on cantilevers using a newly developed spray coating process

The spray coating process have been tested on various polymers - polyvinylpyrrolidone (PVP) and poly (D, L-lactide)

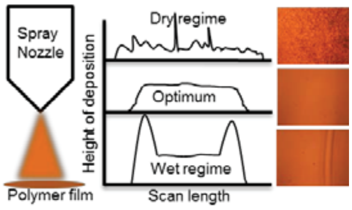


[i] Sanjukta Bose; Stephan S. Keller; Tommy Sonne Alstrøm; Anja Boisen & Kristoffer Almdal: Process Optimization of Ultrasonic Spray Coating of Polymer Films. *Langmuir*, **29**, 6911–6919 (2013)
Sanjukta Bose; Stephan S. Keller; Anja Boisen & Kristoffer Almdal: Cantilever Sensors as a Tool to Measure Enzymatic Degradation of Poly (D, L-lactide) Coatings. *Polymer Degradation and Stability*, **119**, 1-8 (2015)
Sanjukta Bose; Silvan Schmid; Tom Larsen; Stephan S. Keller; Anja Boisen & Kristoffer Almdal: Micromechanical fast quasi-static detection of alpha and beta relaxations with nanograms of polymer. *Journal of Polymer Science, Part B: Polymer Physics*, (2015) *in press*
Sanjukta Bose; Silvan Schmid; Tom Larsen; Stephan S. Keller; Peter Sommer-Larsen; Anja Boisen & Kristoffer Almdal: Micromechanical String Resonators: Analytical Tool for Thermal Characterization of Polymers. *ACS Macro Letters*, **3**, 55-58 (2013)

Getting a uniform sample on the cantilever:

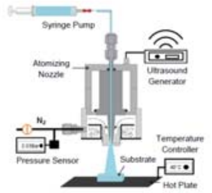
Dry regime - similar to powder arriving at the surface:
- solvent too volatile
- substrate too hot
- spraying nozzle-substrate distance too large

Wet regime - similar to pouring a solution on the substrate:
- solvent not sufficiently volatile
- substrate too cold
- spraying nozzle-substrate

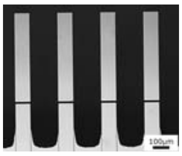


Optimum:
- enough flow to ensure a continuous film.
- Insufficient flow to generate capillary flow mediated accumulation of material at the edge

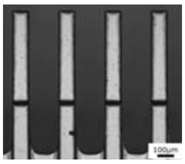
The spraying is accomplished using ultrasonic spray coating. The ultra sound driven nozzle produces very small solution drops



Coating options



Blank cantilevers

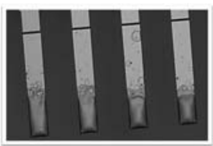


Cantilever coated with ~4µm PDLLA

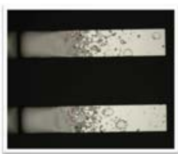
Masks available for:

Partial coating of cantilevers *e.g*

only coated at tip

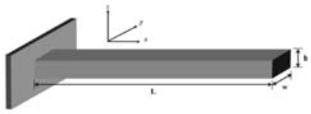


only coated at the base

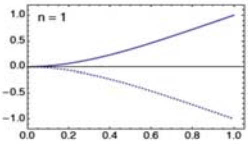


one or two cantilevers out of 8 left uncoated

Cantilever theory - 1



First eigenmode



Within linear elasticity:

$$EI\frac{\partial^4 U(x,t)}{\partial x^4}+\rho A\frac{\partial^2 U(x,t)}{\partial t^2}=0$$

EI (assumed constant): Young's modulus and $I=wh^3/12$

$U(x,t)$: beam displacement

ρ: density; $A=wh$

The eigenfrequencies

$$f_n=\frac{\lambda_n^2}{2\pi}\frac{h}{L^2}\sqrt{\frac{E}{12\rho}}=\frac{1}{2\pi}\sqrt{\frac{k_{eff}}{m_{eff}}}, n=1,2,\ldots$$

λ_n constants representing the eigenfrequencies

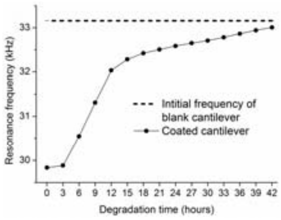
$\lambda_n=c_nL=1.875, 4.694, 7.855,\ldots$; n=1,2,3,…

$k_{eff}=k_{static}\lambda_n^4/12=\lambda_n^4 Ewh^3/(4\times 12L^3)$

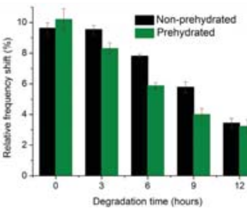
$m_{eff}=\rho whL/4$ to give analogy with the harmonic oscillator

For the cantilevers used here (Micromotive GmbH, Octo500D), silicon 100 surface

E=170 GPa w=90 µm h=5.0±0.3 µm l=470 µm

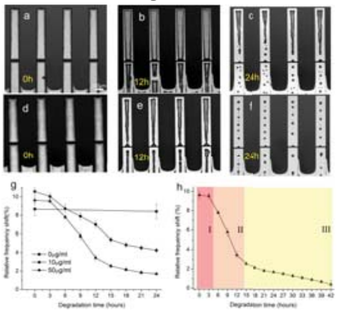


Degradation in 50 µg/ml proteinase K, 37°C. Sample removed from solution for each measurement



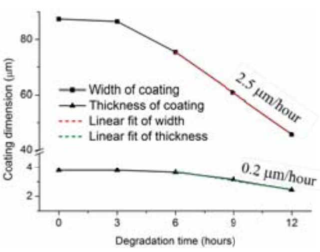
Prehydration: 3 hours in buffer. 50 µg/ml proteinase K solution degradation

Proteinase K degradation of PDLLA

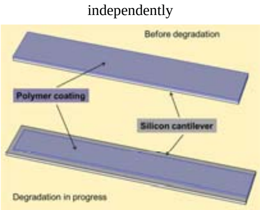


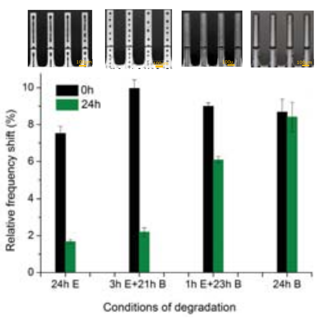
Optical micrographs; proteinase K, 37°C 10 µg/ml (a-c); 50 µg/ml (d-f). all pictures at same scale. 3 regime indicated in h.

Initial delay is followed by rapid degradation. This is apparently due to water swelling kinetics



Finite element modeling of the sandwich structure is used to extract degradation rates for thickness and width of film independently



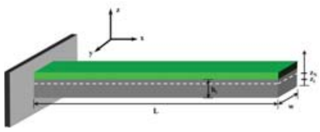


Exposure to enzyme solution followed by buffer.

x h E + y h B: x hours in enzyme solution followed by y hours in buffer

The enzyme will adsorp to the PDLLA film in relatively short time which allow the degradation to continue after washing

Cantilevers theory - 2



A coated cantilever leads to the following modifications:

$$k_{eff}=\sum_i\frac{\lambda_n^4 E_i w h_i (z_n-z_i)^2}{48L^3}=\lambda_n^4\sum_i\frac{E_i I_i}{4L^3}$$

The moments of inertia have to be calculated relative to the neutral (zero strain) plane, z_n.

For $E_{Si}I_{Si} \gg E_{Pol}I_{Pol}$ the neutral plane does not move and k_{eff} is unchanged compare to the uncoated cantilever

Note $E_{Si} \geq 50E_{Pol}$

$$m_{eff}=\frac{Lw}{4}\sum_i\rho_i h_i$$

⇒ **Frequency change dominated by added coating mass**

Conclusions

- An understanding on how to find optimum spray coating conditions for producing uniform micrometer thick films on cantilevers has been established. One needs to be on the borderline between "dry" and "wet" regimes.
- As long as the flexural stiffness of the polymer coat is small compared to the silicon cantilever, the cantilever eigenfrequency is a measure of mass
- The degradation process has an induction period which is due to water swelling kinetics and possibly enzyme absorption kinetics on the polymer
- A versatile platform for fast polymer degradation investigations have been established

Acknowledgements:

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